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Journal:	*The Journal of Physical Chemistry Letters*
Manuscript ID	jz-2019-01005p.R1
Manuscript Type:	Letter
Date Submitted by the Author:	04-May-2019
Complete List of Authors:	Zhang, Jing; Sichuan University, Institute of Atomic and Molecular Physics Li, Lijia; Sichuan University, Institute of Atomic and Molecular Physics Rowell, Nelson ; National Research Council Canada Kreouzis, Theo; Queen Mary University of London, Physics & Astronomy Willis, Maureen; Sichuan University, College of Physical Science and Technology Fan, Hongsong; Sichuan University, Engineering Research Center in Biomaterials Zhang, Chunchun; Sichuan University, Huang, Wen; Sichuan University, West China Hospital Zhang, Meng; Sichuan University, Institute of Atomic and Molecular Physics Yu, Kui; Sichuan University, Institute of Atomic and Molecular Physics; Sichuan University, Institute of Atomic and Molecular Physics

One-Step Approach to Single-Ensemble CdS Magic-Size Clusters with Enhanced Production Yield

Jing Zhang,[†] Lijia Li,[‡] Nelson Rowell,[§] Theo Kreouzis,[Δ] Maureen Willis,[†,Δ]
Hongsong Fan,[‡] Chunchun Zhang,[ζ] Wen Huang,[II]
Meng Zhang,*[,†] Kui Yu*[,†,‡,⊥]

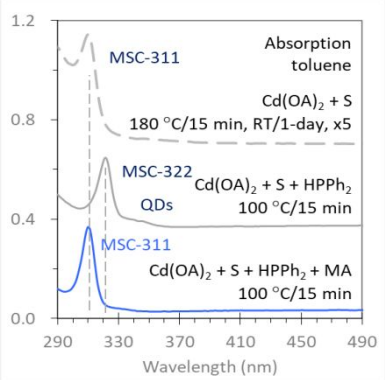
[†]Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, Sichuan, 610065, People's Republic of China
[‡]Engineering Research Center in Biomaterials, Sichuan University, Chengdu, Sichuan, 610065, People's Republic of China
[§]Metrology Research Centre, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada
[Δ]School of Physics and Astronomy, Queen Mary University of London, London, E1 4NS, United Kingdom
[ζ]Analytical & Testing Center, Sichuan University, Chengdu, Sichuan, 610065, People's Republic of China
[II]Laboratory of Ethnopharmacology, West China School of Medicine, Sichuan University, Chengdu, Sichuan, 610065, People's Republic of China
[⊥]State Key Laboratory of Polymer Materials Engineering, Chengdu, Sichuan, 610065, People's Republic of China

M. Z. (email: mengzhang@scu.edu.cn) or to K. Y. (email: kuiyu@scu.edu.cn)

ABSTRACT

We report on the development of a single-step method to synthesize colloidal semiconductor magic-size clusters (MSCs) with an enhanced particle yield in a single-ensemble form and free of the coproduction of conventional quantum dots (QDs). The present process eliminates the need for the second step of a lower-temperature incubation used in a two-step approach reported recently for the fabrication of single-ensemble MSCs without the contamination of QDs. We demonstrate that the combined use of a secondary phosphine (HPR_2) and an α–methyl carboxylic acid ($RCH(CH_3)$–COOH, MA) promotes the yield of MSCs and suppresses the nucleation and growth of QDs. With CdO and elemental S powder as Cd and S sources, respectively, single-ensemble of CdS MSC-311 (displaying sharp absorption peaking at 311 nm) evolves directly in a reaction in 1-octadecene with enhanced production yield. The present study introduces a one-step avenue to synthesize effectively and selectively single-ensemble MSCs, and brings further understanding for the two-pathway model proposed for the prenucleation stage of QDs.

TOC Graphic:



Recently, a two-pathway model was proposed for the induction period that occurs prior to nucleation and growth of colloidal semiconductor II-VI metal (M) chalcogenide (E) quantum dots (QDs).[1] Starting from M and E precursors, one pathway involves the formation of monomers and fragments. This pathway follows the conventional LaMer model of the classical nucleation theory (CNT), which goes forward to nucleation and growth of QDs.[2-4] In the other pathway, precursor compounds (PCs) are formed, which are transparent in optical absorption and can transform to magic-size clusters (MSCs) via an intra-molecular transformation that obeys first-order reaction kinetics.[5,6] The two pathways are connected by an intrinsic MSC to PC to QD pathway, which is consistent with the experimental observation that the growth of QDs is accompanied by the decrease of MSCs.[7-12]

Semiconductor ME MSCs have generally been acknowledged to be side products in the production of colloidal semiconductor ME QDs.[10-12] For samples sequentially extracted from hot-injection or non-hot-injection reaction batches, MSCs display sharp optical absorption peaking usually at particular wavelengths, while QDs exhibit relatively broad optical absorption that continuously redshifts as their size increases. The substantial difference in the absorption linewidth of MSCs and QDs has been attributed to size distribution, which is relatively tight for the former compared to the latter. MSCs display only homogeneous spectral line broadening, while QDs show both homogeneous and inhomogeneous spectral line broadening.[13,14]

Based on the two-pathway model, the selective synthesis of MSCs in a single-ensemble form without the coexistence of conventional QDs has been advanced via a two-step approach.[1,5-8,15] The first step involves the synthesis of the PC of MSCs at a relatively high temperate, and the second step enables the PC to MSC transformation to occur at a relatively low temperature. For example, in the synthesis of single-ensemble CdS MSCs, the first step was performed at 180 °C for about 20 min for the reaction of cadmium oleate ($Cd(OOC–CH_2C_{16}H_{31})_2$, $Cd(OA)_2$) and elemental sulfur (S) in 1-octadecene (ODE). The second step was carried out at a

lower temperature such as room temperature for the PC to MSC transformation. The CdS PC resulted in the first step is transparent in optical absorption at wavelengths longer than 310 nm. When the first-step sample was dispersed in a conventional solvent such as toluene (Tol) at room temperature, CdS MSC-311 evolved during a one-day incubation. The more the PC produced in the induction period at 180 °C from 5 to 20 min, the larger the absorbance detected at 311 nm.[1,5,15] Until now, it has not been known whether it is possible to produce single-ensemble CdS MSC-311 with enhanced yield and without the contamination of QDs. The challenge is apparent, because both pathways could be activated simultaneously at a higher reaction temperature or by more reactive M and/or E precursors (at a lower reaction temperature). In both cases, the MSC yield might be increased, but with QDs produced concurrently.

Herein, we present our exploration on a one-step approach to single-ensemble CdS MSC-311 with enhanced yield and without the coproduction of QDs; this one-step approach precludes the second-step incubation. Our approach involves the combined use of a secondary phosphine such as diphenylphosphine ($HPPh_2$, $HP(C_6H_5)_2$) and one α-methyl carboxylic acid (denoted as MA) such as 2–methyloctadecanoic acid ($C_{16}H_{33}CH(CH_3)–COOH$) or 2–methylbutyric acid ($C_2H_5CH(CH_3)–COOH$). For the conventional reaction of $Cd(OA)_2$ + S in ODE (Scheme 1), the use of a secondary phosphine reduces the temperature required for the formation of Cd and S covalent bonds.[16,17] The addition of α–methyl carboxylic acid in the induction period of the reaction of $Cd(OA)_2$ + S + $HPPh_2$ facilitates the PC to MSC-311 transformation directly in the reaction batch at the evaluated temperature required for the PC formation, and thus suppresses the nucleation and growth of QDs. Figure 1 demonstrates that for the reaction of $Cd(OA)_2$ + S + $HPPh_2$, CdS MSCs evolve at around 100 °C together with QDs (even with a growth period as short as 5 min), although a higher PC yield is obtained than that from the reaction of $Cd(OA)_2$ + S at 180 °C. Figure 2 shows that for the addition of 2–methyloctadecanoic acid in the induction period at 40 °C of the reaction of $Cd(OA)_2$ + S + $HPPh_2$ results in QD-free

single-ensemble CdS MSC-311 with an enhanced cluster yield (at 100 °C over a long growth period of 30 min). Figure 3 illustrates that for the $Cd(OA)_2$ based reactions, the combined use of $HPPh_2$ and an α–methyl carboxylic acid (such as 2–methylbutyric acid) provides a general means to produce single-ensemble CdS MSC-311 selectively and effectively. The exact reason why one α–methyl carboxylic acid facilitates the PC to MSC-311 transformation is a subject for further study. Figure 4 reveals that for the MSC-311 to MSC-322 transformation, MSC-311 obtained from a reaction with 2–methyloctadecanoic acid used is more thermally stable than that without 2–methyloctadecanoic acid. The present study introduces a general one-step approach to colloidal semiconductor MSCs in a single-ensemble form with enhanced production yield and without the coproduction of conventional QDs, and brings further understanding of the two-pathway model proposed.[1]

Figure 1 presents our exploration on the use of a secondary phosphine, $HPPh_2$, to decrease the reaction temperature required for the formation of Cd and S covalent bonds in a conventional reaction of $Cd(OA)_2$ and S in ODE. There are two reactions compared, $Cd(OA)_2$ + S + $HPPh_2$ (Reaction 1, solid traces) and $Cd(OA)_2$ + S (Reaction 2, dashed traces); the feed molar ratio of Cd to S was 4 to 1 and the S concentration was 30 mmol/Kg. For Reaction 1, the S to $HPPh_2$ feed molar ratio was 1 to 4. Each of the two reactions was held at 40 °C for 10 min with one sample taken. Afterwards, the reaction temperature was increased to 100 °C for Reaction 1 and to 180 °C for Reaction 2. Another five samples were collected from each reaction during a reaction period from 5 to 120 min.

The samples with the growth periods of 5 and 30 min are respectively presented in the left (a and c) and right (b and d) panels of Figure 1, and the spectra collected before and after the dispersion incubation are respectively shown in the top (a and b) and bottom (c and d) panels of Figure 1. For the six samples from each of the two reactions, Figure S1-1 shows the evolution of optical absorption properties before and after a dispersion incubation at room temperature for one day. Meanwhile, Figure S1-2 highlights the comparative change in optical absorption

of one sample dispersion before and after the incubation, with Parts a and b for the samples from Reactions 1 and 2, respectively.

For Reaction 1 $Cd(OA)_2$ + S + $HPPh_2$ at 100 °C (solid traces), the five min sample displays a sharp absorption peak at 321 nm is detected (a), suggesting the presence of MSC-322. Furthermore, the presence of a red side shoulder at around 335 nm indicates the presence of QDs. After the incubation (c), a sharp absorption peak at 311 nm is obtained, indicating the evolution of MSC-311. Meanwhile, the population of MSC-322 decreases significantly, appearing as a shoulder of the 311 nm peak. The QDs seem to change little. Similar observations are seen for the 30 min sample. A broad absorption peak at 341 nm suggests the growth of QDs (b); meanwhile, MSC-322 undergoes little change (compared to the five min sample). After the incubation (d), MSC-322 decreases accompanied by the development of MSC-311, and the QDs change little.

For Reaction 2 $Cd(OA)_2$ + S at 180 °C (dashed traces), the absorption spectrum of the five min sample is relatively featureless (a). An absorption peaking at 310 nm evolves after the incubation (c), which suggests the presence of MSC-311. For the 30 min sample, a broad absorption peaking at 355 nm indicates the nucleation and growth of QDs (b). After the one-day incubation, MSC-311 evolves with little change for the QDs (d).

For the conventional reaction of $Cd(OA)_2$ + S in ODE, the temperature required for the formation of Cd–S covalent bond is approximately 160 °C.[1,5,15] For the reaction of $Cd(OA)_2$ + S + $HPPh_2$ in ODE, however, the temperature required is decreased to as low as 40 °C (Figure S1-1). Hence, the evolution behavior of the MSCs in the two reactions is completely different (Figure S1-1). For Reaction 1, MSC-322 evolves during the reaction, without a second step incubation (Figure S1-2a). For Reaction 2, MSC-311 develops only during the second-step incubation at room temperature (for one day) (Figure S1-2b). Depending on the temperature employed in the second step incubation, two types of CdS MSCs can evolve, namely CdS MSC-311 and CdS MSC-322. They have been identified as the first pair of isomers, that

exhibit reversible thermally-induced isomerization for colloidal nanocrystals.[15]

By way of reference, the use of $HPPh_2$ has been reported to result in reactive agents, $SPPh_2H$ and $SePPh_2H$, in the QD synthesis of PbSe,[18,19] PbSeS,[20] ZnSe,[21] ZnSeS,[22] CuInS,[23] and CdSeS.[16,24] Thus, it seems reasonable that the presence of $HPPh_2$ in Reaction 1 leads to the formation of $SPPh_2H$ which is much more reactive than elemental S (as illustrated by Figure S1-3). For this reason, we argue that the presence of MSC-322 in Reaction 1 may be in a similar manner to that reported for a high concentration reaction, which had a S concentration of 500 mmol/Kg with a feed molar ratio of Cd to S of 2 to 1.[25] When the temperature was increased from 120 °C (traces 5 in Figure S1-3) to 160 °C (traces 7 in Figure S1-3), MSC-322 decreased and the CdS QDs kept growing with their absorption peaks from 350 nm to 385 nm (S + $HPPh_2$ batch a) and to 363 nm ($SPPh_2H$ batch b). The disappearance of MSC-322 and growth of QDs is in agreement with the two-pathway model proposed for the formation of QDs and MSCs.[1] Interestingly, during the storage, a MSC-322 to MSC-311 transformation occurs (Figure 1).

Figure 2 contains the results of our investigation on the effect of adding 2–methyloctadecanoic acid (MA) during the induction period at 40 °C of the reaction of $Cd(OA)_2$ + S + $HPPh_2$. Optical absorption data for four reaction batches are presented, which address two reactions of $Cd(OA)_2$ + S + $HPPh_2$ + MA (Reaction 1, solid traces) and $Cd(OA)_2$ + S + $HPPh_2$ (Reaction 2, dashed traces). These reactions were performed with 0.60 mmol of Cd, 0.15 mmol of S, and 0.60 mmol of $HPPh_2$, with a total weight of 5.0 g. Each reaction batch was held for 10 min at 40 °C. For Reaction 1, 1.75 mmol of 2–methyloctadecanoic acid was added after the other three chemicals had been mixed and reacted at 40 °C for 10 min. Each of the two reactions was performed in two ways, namely a temperature increase mode from 60 to 160 °C (top panel) and a constant temperature mode at 100 °C (bottom panel). For the top-panel reactions, a stepwise increment of 20 °C was used and six samples were taken from each batch after the temperature had been held for 10 min at each step. For the bottom-panel reactions, five samples were extracted from each batch

during a reaction period of 5 to 120 min. The results of the last three sample dispersions from the four reaction batches are presented in Figure 2; the data for the remaining sample dispersions are provided in Figure S2-1.

For Reaction 1 $Cd(OA)_2$ + S + $HPPh_2$ + MA, each of the six dispersions made from the 60 to 160 °C samples (top panel solid traces) exhibits a prominent and sharp absorption peak at 311 nm, indicating the presence of MSC-311. Furthermore, the apparent increase of the optical density at 311 nm, from 0.26 for the 60 °C sample to 0.45 for the 160 °C sample, indicates an increase in the population of MSC-311. Moreover, for the 140 and 160 °C samples, a broad and very weak absorption signal was detected respectively peaking at 370 and 410 nm, which designates nucleation and growth of QDs taking place. For the five dispersions made from the 5 to 120 min samples of Reaction 1 at 100 °C (bottom panel solid traces), similar results were observed. The population of MSC-311 increased as shown by the apparent optical density at 311 nm, which increased from 0.31 for the 5 min sample to 0.34 for the 120 min sample. It appears that nucleation and growth of QDs only took place for the 120 min sample, which displays a broad absorption peaking at 354 nm.

For Reaction 2 $Cd(OA)_2$ + S + $HPPh_2$, MSC-322 evolved in the six dispersions made from the 60 to 160 °C samples (top panel dashed traces). Furthermore, the population of MSC-322 increased along the reaction temperature increase up to 100 °C, and decreased afterwards at the higher temperatures. Meanwhile, nucleation and growth of QDs occurred at 80 °C, with broad absorption that shifted from 350 nm for the 120 °C sample to 385 nm for the 160 °C sample. For the five dispersions made from the 5 to 120 min samples of Reaction 2 at 100 °C (bottom panel dashed traces), MSC-322 developed together with QDs. As the reaction progressed, the broad absorption displayed a redshift from 341 nm for the 30 min sample to 357 nm for the 120 min sample.

Figures 2 and S2-1 demonstrate that the addition of 2–methyloctadecanoic acid (MA) (Reaction 1, solid traces) during the induction period of the reaction of $Cd(OA)_2$ + S + $HPPh_2$ is effective in suppressing the nucleation and growth of QDs, as well as in

promoting the formation of MSC-311 without a second-step incubation at a lower temperature. The evolution of MSC-311 instead of that MSC-322 may be related to the fact that the acidity of 2–methyloctadecanoic acid is larger than that of oleic acid (OA).[1] Thus, 2–methyloctadecanoic acid added might interact with the PC by replacing oleic acid. Figure S2-2 shows that the comparison of the optical absorption before and after a one-day incubation at room temperature. For the 120 and 160 °C sample dispersions, evidently, the amount of MSC-311 changed little. This observation suggests that the PC to MSC-311 transformation occurred almost completely at the elevated temperatures for Reaction 1, which involves the combined use of $HPPh_2$ and 2–methyloctadecanoic acid.

Figure S2-3 illustrates that the production yield of the PC in Reaction 1 at 100 °C is increase by ~80%, compared to that in Reaction $Cd(OA)_2$ + S + MA at 180 °C.[1] Meanwhile, prior to the second-step incubation at room temperature, the PC to MSC transformation in the latter reaction was not as complete as that in Reaction 1. Clearly, the combined use of a secondary phosphine (such as $HPPh_2$) and α–methyl carboxylic acid (added in the induction period) is an effective means to synthesize single-ensemble MSCs with enhanced production yield and without the requirement for a second step incubation at a lower temperature.

We now would like to demonstrate that the use of other α–methyl carboxylic acids plays a similar role in facilitating the PC to MSC-311 transformation and in suppressing the formation of QDs. For the formation of M–E covalent bonds at a relatively low temperature in a reaction of M and E precursors with the presence of a secondary phosphine, such as dicyclohexyl phospine ($HP(C_6H_{11})_2$) or $HPPh_2$ ($HP(C_6H_5)_2$), a general proton mediated ligand exchange mechanism has been demonstrated.[17,24] With this in mind, we designed four reaction batches, in which two small-molecule acid additives have been employed (instead of 2–methyloctadecanoic acid) for the two reactions of $Cd(OA)_2$ + S + $HPPh_2$ (a and b) and $Cd(OA)_2$ + S (c and d). The results are illustrated in Figure 3.

These two additives are 2–methylbutyric acid (a and c) and 2,

2–dimethylbutyric acid (b and d). They were added in the induction period at 40 °C for Batches a and b and at 180 °C for Batches c and d, after the temperatures were held for 10 and 15 min, respectively. The first sample was obtained from each of the four batches prior to the addition (dashed traces). After the addition, the reaction temperature for Batches a and b was increased to 160 °C in six steps of 20 °C each. After 10 min held at each step, six samples were taken, and 10 μL of each as-synthesized sample was dispersed in 6.0 mL of toluene for the optical measurements presented in the top panel of Figure 3 (solid traces). For Batches c and d, the reaction temperature was kept at 180 °C; five samples were taken in the additional period of 5 to 120 min, and 25 μL of each as-synthesized sample was dispersed in 3.0 mL of toluene for the optical measurements presented in the bottom panel of Figure 3 (solid traces).

For the addition of 2–methylbutyric acid, a sharp absorption peak at about 311 nm was observed for Samples 2 to 7 of Batch a, which indicates the presence of MSC-311. Furthermore, the amount of MSC-311 increased as the reaction progressed, with enhanced optical density from 0.42 (Sample 2) to 0.71 (Sample 7). At 160 °C, the reaction is still in its induction period prior to the nucleation and growth of QDs. For Batch c, the results obtained are similar to those for Batch a. The population of MSC-311 increased as the reaction proceeded with an optical density of 0.55 for Sample 2 and 0.91 for Sample 6. At 180 °C for up to 120 min, the reaction also remained in its prenucleation stage.

For the addition of 2, 2–dimethylbutyric acid, MSC-311 evolved also for Samples 2 to 7 of Batch b, but with a smaller MSC-311 quantity, compared to that of the corresponding sample from Batch a. Moreover, the onset of nucleation of QDs appeared to occur at 100 °C (Sample 3). Afterwards, the QDs grew in size, as indicated by the redshift of the absorption peak from 399 nm (Sample 4) to 390 nm (Sample 7). The amount of MSC-311 increased slightly from 0.33 (Sample 2) to 0.34 (Sample 3), and then decreased somewhat to 0.32 (Sample 7). For Batch d, similar results are obtained (as those from Batch d). MSC-311 evolved for Samples 2 to 4.

Meanwhile, a broad absorption peak at 385 nm was detected for Sample 2, suggesting the nucleation and growth of QDs. MSC-311 completely depleted for Sample 6, with a pronounced growth of QDs which exhibit a broad absorption peak at 421 nm.

The results presented in Figure 3 demonstrate that the presence of 2–methylbutyric acid (a and c) in the prenucleation stage inhibits the formation of QDs more effectively than that of 2, 2–dimethylbutyric acid (b and d) does. Moreover, both the two small molecules facilitate the PC to MSC-311 transformation at elevated temperatures. For the sample dispersions of Batches a and b presented in Figure 3, Figures S3-1 and S3-2 illustrate a comparison of the optical absorption spectra collected before and after a one-day incubation at room temperature, respectively. After the incubation, there was little change for the amount of MSC-311, which suggests that the PC to MSC-311 transformation was quite complete at elevated temperatures. Accordingly, the combined use of a secondary phosphine (such as $HPPh_2$) and α–methyl carboxylic acid (such as 2-methyloctadecanoic acid or 2–methylbutyric acid added in the induction period) is a general and effective means to synthesize CdS MSC-311 in a single-ensemble form with enhanced production yield and without the necessity of a second-step incubation at a lower temperature.

Given the facts that MSC-322 evolves from the reaction of $Cd(OA)_2$ + S + $HPPh_2$ and that MSC-311 develops with the addition of one α–methyl carboxylic acid (in the induction period at 40 °C), we decided to compare the possible thermally-induced transformations between MSC-311 and MSC-322,[15] which are capped with different surface ligands. To engineer α–methyl carboxylate ligand capped CdS MSCs, we used 2–methyloctadecanoic acid (MA) to directly react with CdO to prepare a Cd precursor $Cd(MA)_2$. Then, we performed the reaction of $Cd(MA)_2$ + S + $HPPh_2$, in the two ways, one with a temperature increase mode from 40 to 160 °C (Figure S4-1) and the other with a constant temperature mode at 100 °C (Figure S4-2). For the former mode as shown in Figure S4-1, MSC-311 evolved from the reaction batch, and the nucleation and growth of QDs was suppressed even at a temperature as high

as 140 °C. Simultaneously, the amount of MSC-311 monotonically increased up to 140 °C. For the latter mode as shown in Figure S4-2, MSC-311 kept increasing monotonically in the induction period up to 120 min monitored. Furthermore, the PC to MSC-311 transformation appeared quite complete, as indicated by little change monitored in optical absorption after the one-day incubation at room temperature.

Now, let us compare the thermal stability for the CdS MSCs capped by the different ligands, according to the thermally-induced isomerization between MSC-311 and MSC-322 reported.[15] They are MSC-322 capped by oleate ligands synthesized from the reaction of $Cd(OA)_2$ + S + $HPPh_2$, and MSC-311 capped by 2–methyl carboxylate ligands prepared from the reaction of $Cd(MA)_2$ + S + $HPPh_2$. Figure 4 shows the optical absorption spectra collected from two samples, one from the $Cd(OA)_2$ + S + $HPPh_2$ reaction (a) and the other from the $Cd(MA)_2$ + S + $HPPh_2$ reaction (b). The two samples were extracted at 100 °C with a growth period of 5 min. Each sample (10 μL) was dispersed in 6.0 mL of toluene, and the optical measurements were performed immediately (blue traces), after a one-day incubation at room temperature (green traces), and with further incubation at 40 °C for 2 hours (red traces).

For the $Cd(OA)_2$ + S + $HPPh_2$ reaction product shown in Figure 4a, a sharp absorption peak at 321 nm is observed (blue trace), indicating the presence of oleate capped MSC-322. After the room temperature incubation, the presence of a new sharp peak at 311 nm suggests the evolution of MSC-311, with a significantly decreased quantity for MSC-322 (green trace). After the 40 °C incubation, MSC-322 reformed and MSC-311 disappeared (red trace). For the $Cd(MA)_2$ + S + $HPPh_2$ reaction product shown in Figure 4b, MSC-311 formed initially displaying a sharp absorption peak at 307 nm (with an optical density of 0.32, blue trace). After the room temperature incubation, a little change was detected for MSC-311 with an optical density of 0.37 and peaking at 308 nm (green trace). After the 40 °C incubation, the absorption peak shifted to 313 nm, but with MSC-322 not evident (red trace). For the absorption peak positions of MSC-311 shown in Figure 4b, it may

be of help to point out that during the evolution of MSC-311 from its PCs (in cyclohexane for two days), the redshift from 302 to 311 nm has been documented.[5] Also, the peak position is affected by dispersion environments including temperatures, such as a few nanometer redshifts for CdSe MSC-415 at 30 to 60 °C.[9]

Accordingly, MSC-311 capped by α–methyl carboxylate ligands (resulted from the $Cd(MA)_2$ + S + $HPPh_2$ reaction) did not display a thermally-induced transformation to CdS MSC-322, as readily as MSC-311 capped by oleate ligands did, which was from the $Cd(OA)_2$ + S + $HPPh_2$ reaction. This may be reasonably attributed to the fact that 2–methyloctadecanoic acid has a stronger coordination effect towards Cd than oleic acid does.[1] Thus, α–methyl carboxylate capped MSC-311 (Figure 4b) displayed a higher thermal stability than oleate capped MSC-311 (Figure 4a). By a side note, the reactivity of $Cd(OA)_2$ is higher than that of $Cd(MA)_2$, and the PC produced from a $Cd(OA)_2$ + S reaction batch at 180 °C (with a growth period of 15 min) seemed to be more than that from a $Cd(MA)_2$ + S reaction batch at 200 °C (with the same growth period of 15 min).[1]

In conclusion, we have demonstrated that it is possible to tune the pathways proposed in the two-step model for the prenucleation stage of colloidal semiconductor ME QDs.[1] Via the combined use of a secondary phosphine and an α–methyl carboxylic acid, we have developed an effective and selective one-step approach to single-ensemble CdS MSCs free of QDs and with enhanced production yield. The use of a secondary phosphine (such as $HPPh_2$) improves the precursor reactivity and thus decreases the temperature required for the formation of the PCs and promotes the PC yield. For a $Cd(OA)_2$ + S + $HPPh_2$ reaction, the coproduction of both MSCs and QDs is almost unavoidable even at temperatures as low as 80 °C. The use of an α-methyl carboxylic acid in the induction period (prior to nucleation and growth of QDs in a reaction batch of $Cd(OA)_2$ + S + $HPPh_2$) facilitates the PC to MSC-311 transformation at elevated temperatures and thus suppresses the nucleation and growth of QDs. Upon the α–methyl carboxylic acid (MA) addition, such as 2–methylbutyric acid or 2–methyloctadecanoic acid, during the induction period at

40 °C, the formation of QDs is suppressed even at temperatures as high as ~140 °C. Meanwhile, the PC to MSC-311 transformation is also facilitated under such temperatures without a second-step incubation at a lower temperature, which is required for the two-step approach reported.[5] The combined use of a secondary phosphine and an α–methyl carboxylic acid results in a significant overlap in the temperature range required for the PC formation (Step 1) as well as for the PC to MSC transformation (Step 2), making a one-step approach to single-ensemble MSC production possible. Interestingly, the thermal stability of 2–methyl carboxylate capped MSC-311 is higher than that of oleate capped MSC-311; thus, the thermally-induced MSC-311 to MSC-322 transformation for the former does not occur as readily as it does for the latter. The effect of an α–methyl carboxylic acid on the PC to MSC-311 transformation is a promising avenue for further study. The present approach is applicable to CdSe and CdTe MSCs, and we are actively optimizing synthetic conditions for these systems. We would like to point out that the reaction of $Cd(OA)_2$ + E + $HPPh_2$ + MA (with MA = 2–methylbutyric acid) is preferred, due to cost as well as the difficulty in the preparation of $Cd(MA)_2$. The present study provides additional insight into the two-pathway model proposed recently.[1] The collective effort on the synthesis and formation pathway has been moving the field of colloidal semiconductor clusters and nanocrystals one-step forward to transform from an empirical art to science, similar to the advance of organic chemistry.[26-37]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: xxx

Experimental details including synthesis and characterization information with additional optical absorption spectra (PDF)

AUTHOR INOFRMATION

Corresponding Authors

*E-mail: mengzhang@scu.edu.cn

*E-mail: kuiyu@scu.edu.cn

ORCID

Nelson Rowell: 0000-0001-7616-9396

Hongsong Fan: 0000-0003-3812-9208

Meng Zhang: 0000-0002-2852-2527

Kui Yu: 0000-0003-0349-2680

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

K. Y. thanks the National Natural Science Foundation of China (NSFC) 21773162 and 21573155, the State Key Laboratory of Polymer Materials Engineering of Sichuan University (Grant No. sklpme2018-2-08), the Open Project of Key State Laboratory for Supramolecular Structures and Materials of Jilin University for SKLSSM 201935, and the Fundamental Research Funds for the Central Universities. M. Z. thanks the Sichuan University Postdoctoral Fellowship 2019SCU12073. H. F. and W. H. thank the National Major Scientific and Technological Special Project for "Significant New Drugs Development" (2018ZX09201009-005-004 and 2018ZX09201009-005-001).

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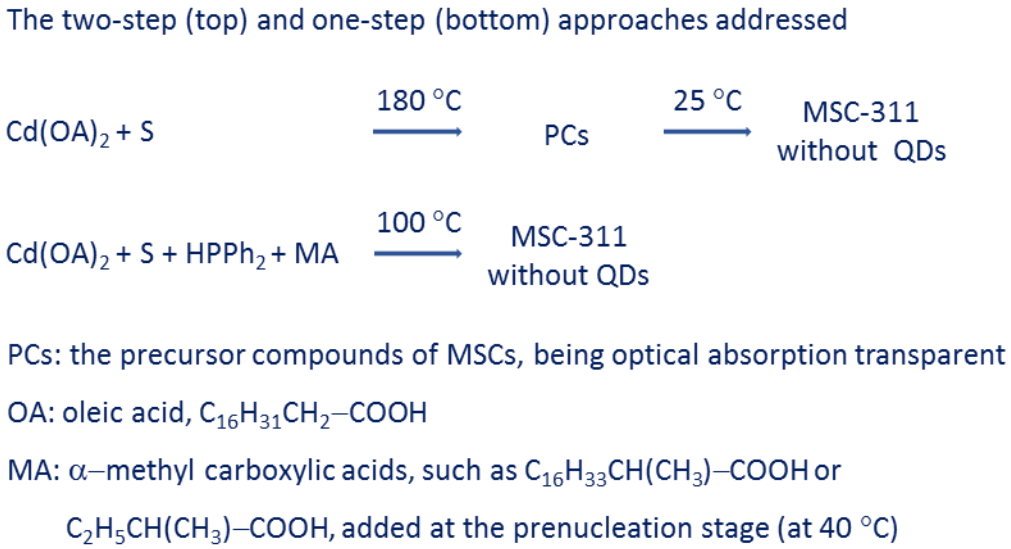

Scheme 1. Schematic drawing illustrating the formation of CdS MSC-311 by either a two-step approach (Reaction $Cd(OA)_2$ + S) or a one-step approach (Reaction $Cd(OA)_2$ + S + $HPPh_2$ + MA). In the two-step approach (top), the PC formation occurs at a relatively high temperature (such as 180 °C), and the PC to MSC-311 transformation takes place at a relatively low temperature (such as room temperature 25 °C). In the one-step approach (bottom), the PC formation occurs at an intermediate temperature (such as 100 °C), together with the PC to MSC-311 transformation. For the one-step approach, which involves the combined use of a secondary phosphine and one α-methyl carboxylic acid, the production yield of single-ensemble MSC-311 free of QDs is higher than that from the conventional two-step approach (top).

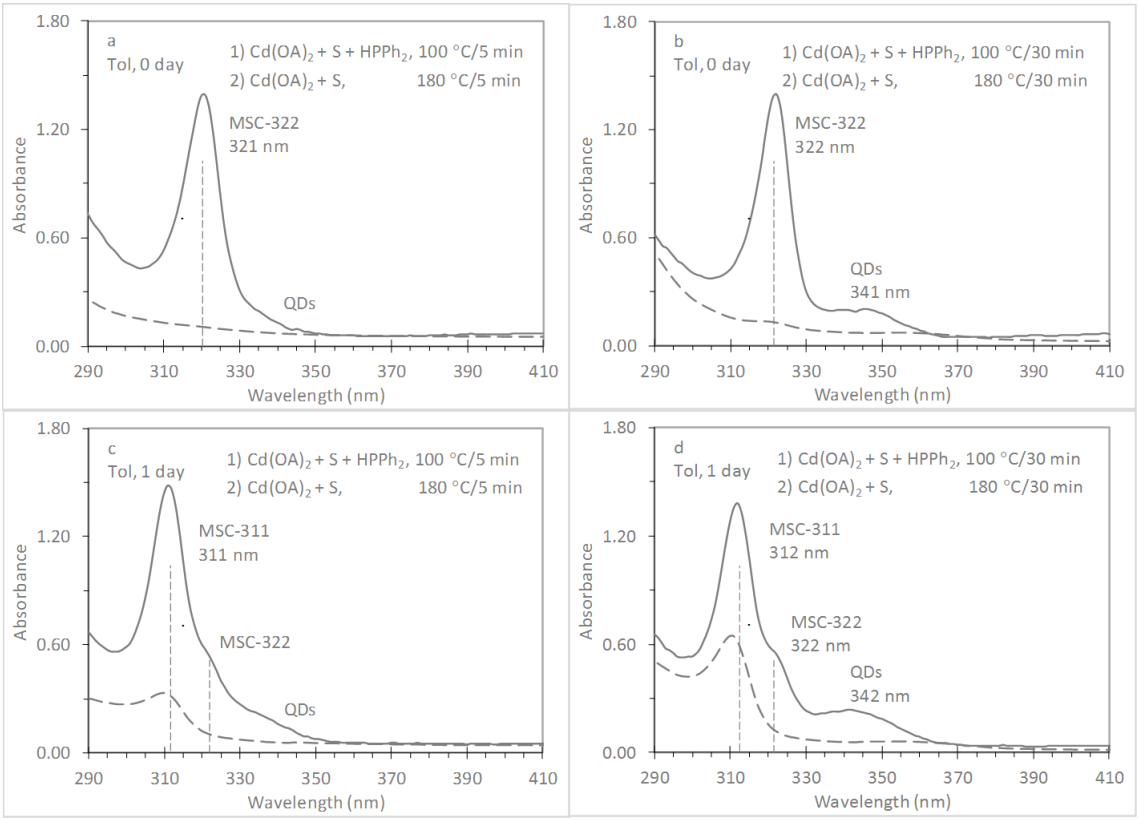

Figure 1. Effect of the use of a secondary phosphine $HPPh_2$. Optical absorption spectra of four as-synthesized samples from the reaction of $Cd(OA)_2$ + S + $HPPh_2$ at 100 °C (1, solid traces) and of $Cd(OA)_2$ + S at 180 °C (2, dashed traces). The total weight of each of the reactions was 5.0 g, with 0.60 mmol of Cd and 0.15 mmol of S. The former reaction had 0.60 mmol of $HPPh_2$. The reaction periods were 5 (a and c) and 30 min (b and d), as indicated. The samples (10 µL each) from Reaction 1 were dispersed in 6.0 mL of toluene, and those (25 µL each) from Reaction 2 were dispersed in 3.0 mL of toluene. The absorption measurements were performed before (a and b) and after (c and d) a room-temperature incubation for one day. The four solid traces are multiplied by a factor of five, to compare with the corresponding dashed spectra. Evidently, the production yield of MSCs for Reaction 1 at 100 °C is higher than that for Reaction 2 at 180 °C, but with the coproduction of QDs.

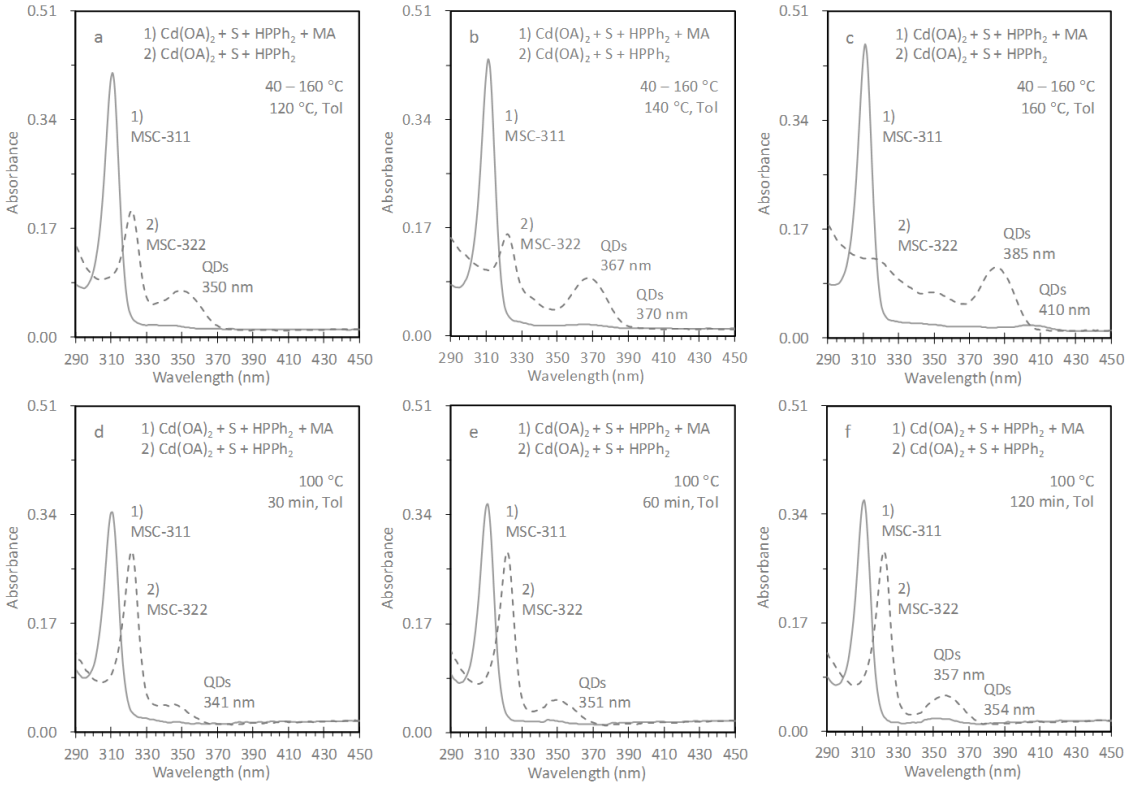

Figure 2. Exploration of the addition of an α-methyl carboxylic acid in the induction period of the formation of QDs. Optical absorption spectra of samples from the reactions of $Cd(OA)_2$ + S + $HPPh_2$ + MA (1, solid traces) and $Cd(OA)_2$ + S + $HPPh_2$ (2, dashed traces). For Reaction 1, MA was added in the induction period at 40 °C after the temperature was held for 10 min. Both reactions were carried out either with a temperature increase from 40 to 160 °C (top panel) or with a constant temperature at 100 °C (bottom panel). For the top panel, the samples were extracted after 10 min at 120 (a), 140 (b), and 160 °C (c). For the bottom panel, the samples were taken with the reaction period of 30 (d), 60 (e), and 120 min (f). An aliquot (10 μL) of each sample was dispersed in toluene (6.0 mL) for the measurement. It is apparent that the addition of MA in the induction period suppresses the evolution of QDs (Reaction 1), as compared to Reaction 2.

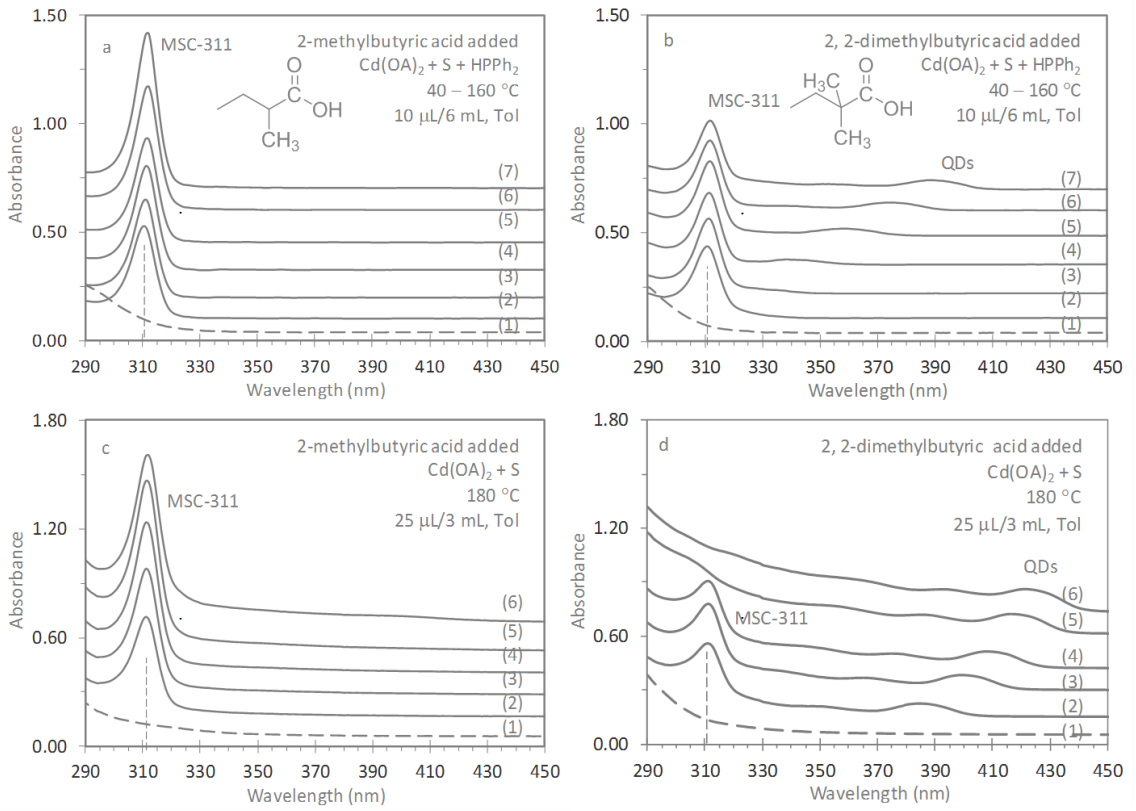

Figure 3. Investigation of the effect of other α–methyl carboxylic acids instead of MA. 2–methylbutyric acid (a and c) and 2, 2–dimethylbutyric acid (b and d) were respectively added in the induction period at 40 °C after 10 min for the $Cd(OA)_2$ + S + $HPPh_2$ reaction (a and b), or at 180 °C after 15 min for the $Cd(OA)_2$ + S reaction (c and d). Before the addition, a sample was obtained from each batch (dashed traces); after the addition, the reaction temperature was increased to 160 °C in steps of 20 °C each (a and b) or kept at 180 °C (c and d). From Batches a and b, another six samples were collected after 10 min held at (2) 60, (3) 80, (4) 100, (5) 120, (6) 140, and (7) 160 °C; 10 µL of each sample was dispersed in 6.0 mL of toluene. From Batches c and d, another five samples were extracted at (2) 5, (3) 15, (4) 30, (5) 60, and (6) 120 min; 25 µL of each sample was dispersed in 3.0 mL of toluene. The results of the optical absorption spectra collected suggest that 2–methylbutyric acid (a and c) inhibits the formation of QDs more effectively than 2, 2–dimethylbutyric acid (b and d) does.

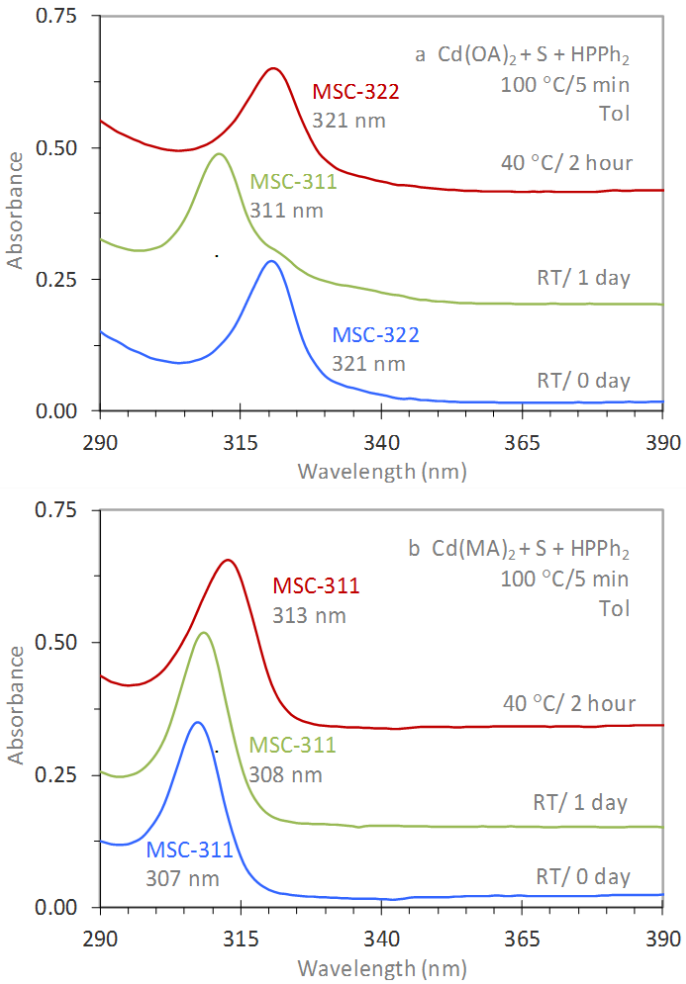

Figure 4. Examination of the thermal stability of MSC–311 capped by different surface ligands via the possible thermally-induced transformation between MSC-311 and MSC-322. Two samples were extracted from the reaction batches of $Cd(OA)_2$ + S+ $HPPh_2$ (a) and $Cd(MA)_2$ + S+ $HPPh_2$ (b) at 100 °C for 5 min. An aliquot (10 μL) of each sample collected was dispersed in toluene (6.0 mL) for the optical absorption measurements, before (blue traces) and after (green traces) a room temperature incubation for one day, followed by a further incubation at 40 °C for 2 hours (red traces). The MSC-311 to MSC-322 transformation at 40 °C is more readily for oleate ligand capped MSC-311 (a) than for 2–methyl carboxylate ligand capped MSC-311 (b); thus, the thermal stability of the latter is higher than that of the former.